

University of Wollongong

Research Online

University of Wollongong Thesis Collection
1954-2016

University of Wollongong Thesis Collections

2006

Distribution, speciation and geochemistry of selenium in contaminated marine sediments - Port Kembla Harbour, NSW, Australia

Pattanan Tarin

University of Wollongong

Follow this and additional works at: <https://ro.uow.edu.au/theses>

University of Wollongong

Copyright Warning

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site.

You are reminded of the following: This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author. Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material.

Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.

Recommended Citation

Tarin, Pattanan, Distribution, speciation and geochemistry of selenium in contaminated marine sediments - Port Kembla Harbour, NSW, Australia, PhD thesis, School of Earth & Environmental Sciences, University of Wollongong, 2006. <http://ro.uow.edu.au/theses/714>

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

NOTE

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

**DISTRIBUTION, SPECIATION AND GEOCHEMISTRY OF
SELENIUM IN CONTAMINATED MARINE SEDIMENTS -
PORT KEMBLA HARBOUR, NSW, AUSTRALIA**

A thesis submitted in fulfillment of the requirements for the
award of the degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

PATTANAN TARIN

(BSc Hons)

SCHOOL OF EARTH AND ENVIRONMENTAL SCIENCES

- 2006 -

Certification

I, Pattanan Tarin, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the School of Earth and Environmental Sciences, University of Wollongong, is my own work unless otherwise referenced or acknowledged. The thesis has not been submitted for a degree at this or any other academic institution.

.....

Pattanan Tarin (Author)

.....

(Date)

Acknowledgements

I would like to express my gratitude to the following people who have helped and supported me during the course of this research:

- My supervisors: Prof John Morrison (*Uni dad*) and Dr Dianne Jolley (*Uni sister*) for their guidance, encouragement and understanding, and all other support, especially with the intense proofreading during the final stage.
- Royal Thai Government for the scholarship support and Port Kembla Copper Ltd. (PKC) for the first year project funding.
- Drs Glennys O'Brien, Damris Muhammad and Bryan Chenhall for sharing knowledge on sediment chemistry. Prof Bill Maher (UC) and Drs Stuart Simpson and Rob Jung (CSIRO Lucas Heights) for comments and advice on selenium and sediment work.
- Tonnes of thanks to Mark O'Donnell for all the technical help and a very hard work during several core-sampling trips, and to Geoff Black for help with boat preparation.
- Chris Chipeta (PKC) for prompt processing of numerous samples and support during the first year harbour survey. Leigh Lemmon (PKC) and Louis Whant (Bluescope Steel) for the labour work during collection of the grab samples. Captain Chris Haley and staff (Port Kembla Port Corporation) for the grab-sampling boat service.
- Atun Zawadski, Jennifer Harrison and Helen at ANSTO for help with the sediment dating work. Thanks also to AINSE for providing the grant funding.
- Sandra Quin, Marina, Jenny, Louisa and Wendy for administrative support, Pam Morgan, Sue and Cathy, Heidi Brown, Peter Haines, Peter Sara, John Korth and the TO team for technical and miscellaneous help. Special thanks are extended to Beth Peisley – the Faculty Librarian, and Darien – a student service counselor.
- Angel friends who have shared life outside Uni and kept me well during this time: P'Nang and Charles Pasfields (foster friends); Vivian, Ava, Perl and postgrad lady support group; Jolley's and Morrison's past and present students; Sim Fui, Michi, Minh Hue and many generations of flat mates; SGI and AusaidGang friends; my brother – Suwat, my sister and nieces – Arunsri, little Yoa-Yoa and Yoke.

Finally, to god and my parents who provide me love and righteousness. Not having had opportunity to be formally educated and not knowing any English, both parents will be looking at this thesis like a work of an alien species but would be so over the moon to have a daughter called 'doctor' which will be cool.

Abstract

Selenium (Se) is an element of concern in Port Kembla Harbour as it was the only element found in harbour fish tissues in the mid-1990s at concentrations that exceeded the Australia New Zealand Food Authority Maximum Residue Limit. This thesis investigated the distribution, speciation, binding phases and geochemical behaviour of selenium in Port Kembla Harbour sediments, which potentially receive selenium pollution from local metal processing and smelting and coal industries. Sedimentary selenium is a potential selenium source for fish and organisms via benthic food chain transfer.

Grab surface sediments from 23 sites around the harbour and a total of 14 sediment cores were collected from the contaminated Red Beach area (during 2003-2006) and analysed for selenium concentrations by HG-AAS and also for sediment parameters including grain size composition, pH, redox potential, other trace metals, porewater composition and sediment macrocomponents. Two sequential extraction procedures were used to fractionate the solid-phase selenium into soluble and adsorbed, carbonate, metal oxyhydroxide, organically bound, elemental, organic matter and sulfide, and residual selenium fractions. The selenium behaviour in the different geochemical phases was examined in association with the measured sediment parameters.

The selenium concentrations in surface sediments from most harbour sites were low (below 3 $\mu\text{g/g}$) except those in sediments from the Red Beach area (up to 9.38 $\mu\text{g/g}$), which is in close proximity to a local copper refinery. Selenium concentrations in the Red Beach sediment cores ranged from 6 to 1735 $\mu\text{g/g}$, depending on depth and grain size, with peak selenium concentrations observed at 6-10 cm and at 14-16 cm depths. The highest selenium concentration (1735 $\mu\text{g/g}$), found in the $<63\ \mu\text{m}$ Red Beach sediments, was 100 times higher than the highest sedimentary selenium concentration previously reported in Australia. The sedimentary selenium was concentrated in fine ($<63\ \mu\text{m}$) grains that are easily mobile. Selenium was correlated mainly with Pb, Cu and Zn in the $>250\ \mu\text{m}$ fraction of the surface sediments and in the $<63\ \mu\text{m}$ fraction of the sediment cores, indicating association from both original ore sources and through post-depositional transformation. The sediment ^{210}Pb dating estimated the sedimentation rate of Red Beach cores to be $0.55 \pm$

0.03 cm/year. Sediment ^{210}Pb dating provided an indication that the deeper sediments were not disturbed and high selenium concentrations in the sediment cores were a result of historical selenium input potentially from a copper smelter.

The solid-phase selenium in the Red Beach sediment cores was present mainly as elemental selenium. High proportions of the selenium were also bound to the organic matter in the upper 10 cm region and associated with the residual fraction below 10 cm. Selenite was the major selenium species found in the organically bound selenium fraction. Small proportions of the solid-phase selenium were in soluble and adsorbed fractions, with peak concentrations in the below 10 cm depth region. Minimal amounts of selenium were found to associate with iron-manganese oxyhydroxides and carbonate minerals in the sediment.

The Red Beach sediment cores were oxic in the top 2 cm and anoxic below 2 cm depths. The top 2 cm oxic sediment contained low solid-phase selenium concentrations and low porewater selenium concentrations. The anoxic 2-10 cm core region contained the peak solid-phase selenium concentrations but with low porewater selenium concentrations. This layer was enriched with the organic matter, AVS, organically bound selenium, and elemental selenium species, indicating a strong link between organic matter decay processes and the reduction of sulfate and selenium. The below 10 cm-anoxic sediments contained moderate solid-phase selenium, peak porewater selenium and high soluble and adsorbed selenium concentrations, and stable pyritic sulfur species. Selenium was observed to become associated with the residual fraction at the expense of the organically bound and the elemental selenium in this region. This below 10 cm region contained lower proportions of copper, lead and zinc in the residual fraction but significant amounts in the organically bound fractions. The solid-phase selenium correlated with the solid-phase sulfur through the association of their reduced forms: elemental selenium, pyrite and possibly as pyritic selenium. Copper was the only major element that co-extracted with elemental selenium. The reduced selenium forms (elemental and residual) correlated significantly with Cu, Pb and Zn, suggesting possible formation of independent CuSe , PbSe and ZnSe minerals in the sediment. Redox potential, sedimentation rate, organic matter components, sulfur and transition elements are concluded to be the important factors affecting the selenium geochemical behaviour in Red Beach cores.

Table of Contents

Certification.....	ii
Acknowledgements.....	iii
Abstract.....	iv
Table of Contents.....	vi
List of Figures.....	xi
List of Tables.....	xv
Abbreviations.....	xix

Chapter 1:

Introduction

1.1	General introduction.....	1
1.2	Port Kembla Harbour study site.....	3
1.3	Objectives of this study.....	5
1.4	Thesis outline.....	6

Chapter 2:

Literature review of selenium in the aquatic environment

2.1	Introduction.....	7
2.2	Selenium.....	7
2.2.1	Properties.....	7
2.2.2	Production and uses.....	8
2.3	Environmental sources and occurrence of selenium.....	11
2.4	Selenium distribution in Australian aquatic environments.....	13
2.4.1	Water.....	13
2.4.2	Sediment.....	14
2.4.3	Organisms.....	17
2.5	Biological uptake.....	20

2.5.1	Water-borne selenium pathway.....	20
2.5.2	Particulate and sedimentary selenium.....	21
2.5.3	Dietary pathway.....	22
2.6	Selenium toxicity.....	23
2.6.1	Aquatic life.....	23
2.6.2	Wildlife and animals.....	24
2.6.3	Human.....	25
2.6.4	Toxicity mechanism.....	25
2.7	Selenium biogeochemical processes.....	27
2.7.1	Speciation.....	28
2.7.2	Sorption and precipitation.....	30
2.7.3	Coupled redox processes.....	31
2.7.4	Microbial activities.....	33
2.8	General conclusions.....	34

Chapter 3:

Evaluation and optimisation of a rapid method for total selenium determination in marine sediments using microwave digestion and hydride generation-atomic absorption spectrometry

3.1	Introduction.....	35
3.2	Materials and methods.....	38
3.2.1	Reagents and glassware.....	38
3.2.2	Microwave digestion procedures.....	38
3.2.3	Sample pretreatment for HG-AAS analysis.....	40
3.2.4	Selenium determination by HG-AAS.....	41
3.3	Results and discussion.....	43
3.3.1	Evaluation of microwave digestion methods.....	43
3.3.2	Reduction of selenate to selenite.....	45
3.3.3	Elimination of nitrogen oxide interferences.....	47
3.3.4	Analytical performance.....	48
3.4	Conclusions.....	51

Chapter 4:

Selenium speciation in marine sediment extracts using high performance liquid chromatography and hydride generation-atomic absorption spectrometry

4.1	Introduction.....	52
4.2	Materials and methods.....	56
4.2.1	Reagents and apparatus.....	56
4.2.2	Test materials.....	58
4.2.3	Sediment extraction procedure.....	59
4.2.4	HPLC separation and selenium detection.....	60
4.3	Results and discussion.....	61
4.3.1	Sediment extraction.....	61
4.3.1.1	Effects of extractant reagents on HG-AAS detection.....	61
4.3.1.2	Choice of extractants.....	63
4.3.1.3	Effects of extractant concentration and extraction time.....	65
4.3.2	Optimisation of the HPLC separation.....	67
4.3.3	Application to sediment NaOH extracts.....	71
4.4	Conclusions.....	73

Chapter 5:

Selenium distribution in Port Kembla Harbour sediments

5.1	Introduction.....	74
5.2	Materials and methods.....	75
5.2.1	Reagents and apparatus.....	75
5.2.2	Collection of surface sediments and core samples.....	75
5.2.3	Sample preparation and analysis for selenium.....	78
5.2.4	Lead-210 dating of Red Beach sediment cores.....	80
5.3	Results and discussion.....	83
5.3.1	Selenium in surface sediments.....	83
5.3.1.1	Sediment characteristics and grain size.....	83
5.3.1.2	Selenium spatial distribution.....	84
5.3.1.3	Selenium distribution in different grain sizes.....	87

5.3.1.4	Relationships with other trace elements.....	87
5.3.1.5	Preliminary hazard assessment.....	92
5.3.2	Selenium in Red Beach sediment cores.....	94
5.3.2.1	Sediment core characteristics and pH.....	94
5.3.2.2	Sediment ^{210}Pb dating results.....	94
5.3.2.3	Selenium distribution in sediment cores.....	97
5.3.2.4	Relationships with other elements in core sediments.....	100
5.3.2.5	Factors affecting the selenium vertical distribution.....	104
5.4	Conclusions.....	106

Chapter 6:

Geochemistry of selenium in contaminated marine sediments – Red Beach, Port Kembla Harbour

6.1	Introduction.....	107
6.2	Materials and methods.....	114
6.2.1	Reagents and apparatus.....	114
6.2.2	Sample collection and analysis.....	115
6.2.3	Sequential extraction procedures.....	120
6.3	Results and discussion.....	123
6.3.1	Sediment characteristics, redox potential and pH.....	123
6.3.2	Sediment porewater compositions.....	125
6.3.2.1	Porewater sulfate and phosphate.....	125
6.3.2.2	Porewater selenium.....	127
6.3.3	Macrocomponent depth profiles.....	129
6.3.4	Forms and binding phases of selenium in Red Beach sediments.....	136
6.3.4.1	SEP 1 fractionation.....	136
6.3.4.2	SEP 2 fractionation.....	140
6.3.5	Selenium geochemical behaviour in Red Beach sediments.....	146
6.3.6	Implications for potential remobilization and bioavailability.....	150
6.4	Conclusions.....	151

Chapter 7:**Conclusions and recommendations**

7.1	Introduction.....	152
7.2	Conclusions.....	152
7.3	Recommendations for future research.....	156

References.....	152
------------------------	------------

Appendix A Surface sample data.....	I
--	----------

Appendix B Core sample data.....	VIII
---	-------------

List of Figures

Figure 1.1	Port Kembla Harbour, NSW, showing major drains and surrounding industrial environments.....	4
Figure 1.2	Selenium studies in Port Kembla Harbour sediments, highlighting the topics covered in each of the main thesis chapters.....	6
Figure 2.1	Selenium cycling in aquatic environment.....	27
Figure 2.2	A phase diagram for the Se-H ₂ O system for pH and redox potential (Eh). Between two solid lines is the stability region of water.....	28
Figure 2.3	A schematic of zones of organic matter degradation during diagenesis processes in sediments.....	32
Figure 3.1	In-house microwave rotators for multi-sample digestion, fitted general 50-mL centrifuge tubes.....	39
Figure 3.2	Selenium analysis by HG-AAS using Varian VGA-76 vapour generator....	42
Figure 3.3	Typical HG-AAS calibration curve for selenium.....	49
Figure 3.4	HG-AAS response of selenite standard added to 10 % nitric digested samples (containing 40% HCl, 4% HNO ₃ and 0.16% urea), measured against 40% HCl calibration standards.....	50
Figure 4.1	Structures and pK _a values of four selenium compounds studied.....	54
Figure 4.2	Effects of extractant matrix on HG-AAS signal (mean ± SE, n=3). HCl, Ascorbic acid, H ₃ PO ₄ , H ₃ PO ₄ : Methanol, NH ₂ OH.HCl and NaOH were 0.5 mol/L. KCl was 0.25 mol/L and phosphate (pH 8) was 0.1 mol/L.....	62
Figure 4.3	Percentage (mean ± SE, n = 3) of selenium extracted from test sediments by different extractant reagents: HCl, H ₃ PO ₄ and NH ₂ OH.HCl were 0.5 mol/L, KCl was 0.25 mol/L, and NaOH and Phosphate (pH 8) were 0.1 mol/L.....	63
Figure 4.4	Intense brown colour of NaOH extracts of SRM 2702, in comparison to (a) other reagent extracts of SRM 2702: hydrochloric acid, phosphoric acid, phosphoric: methanol and hydroxylamine hydrochloride; and (b) sodium hydroxide extracts of other test sediments from Port Kembla Harbour: wet anoxic, PKH-1 and Red Beach (19b) sediments.....	64
Figure 4.5	Percentage of selenium extracted in sodium hydroxide solutions with different extraction time from (a) SRM 2702 and (b) wet anoxic sediment	66

Figure 4.6	HPLC of standard selenium compounds (0.1 $\mu\text{g Se}$) (a) in MilliQ water, and (b) in 0.1 mol/L NaOH solutions. Hamilton PRP-X100 anion exchange column, 40 mM /200 mM ammonium phosphate buffer, pH 6 mobile phase.....	68
Figure 4.7	HPLC of sediment NaOH extracts: (a) oxic Red Beach sediment (0.1 mol/L, 12 hour extraction) and (b) anoxic wet sediment (0.1 mol/L, 4 hour extraction), Hamilton PRP-X100 anion exchange column 40 mM /200 mM ammonium phosphate buffer, pH 6, mobile phase.....	71
Figure 5.1	Locations of surface samples collected from 23 sites around Port Kembla Harbour on 7 th April 2003.....	76
Figure 5.2	Laboratory set up for sediment sample processing. From right to left, sediment core samples, nitrogen glove box and sediment core extruder.....	77
Figure 5.3	Sample preparation and analysis flowchart for selenium spatial distribution studies in Port Kembla Harbour sediments.....	79
Figure 5.4	Dominant grain size distribution in surface sediment samples.....	83
Figure 5.5	Spatial distribution of selenium ($\mu\text{g/g}$, d.w.) in surface sediments from Port Kembla Harbour (a) whole sediments and (b) < 63 μm fractions.....	85
Figure 5.6	Selenium concentrations (dry weight) in surface sediments from 23 sites of Port Kembla Harbour (a) $\mu\text{g Se/g}$ for each individual grain size fraction, data points with error bars were means of oxic and anoxic results and those with no error bars were of composite samples (b) $\mu\text{g Se}$ in 1 gram of whole sediment as a function of each grain size.....	88
Figure 5.7	Correlations between selenium and several trace elements in whole surface sediments of Port Kembla Harbour, excluding Sites 18, 19 and 20.....	89
Figure 5.8	Selenium concentrations in whole surface sediments from Port Kembla Harbour. The red line indicates the 4- $\mu\text{g/g}$ biological effect threshold, as suggested by the USA research guidelines.....	92
Figure 5.9	Pb-210 dating of Core C4 and Core D1 (top) plots of excess Pb-210 activity (Bq/kg), normalized with < 63 μm grain size, against depth (bottom) sediment age calculated from CIC model.....	96
Figure 5.10	Grain size distribution and total selenium in three Red Beach sediment cores	98
Figure 5.11	Depth concentration profiles of selenium and other trace elements in Red Beach (<63 μm) sediments, Cores A1-A3.....	101

Figure 5.12	Vertical profiles of selenium concentrations (mean \pm SE) in Red Beach sediment cores (Cores B1-6 and C1-4 data are taken from Chapter 6). The corresponding sediment age (Year) determined from ^{210}Pb dating is plotted against the annual refined copper production by ER&S/SCL.....	105
Figure 6.1	Sediment core sample preparation and analysis flowchart.	117
Figure 6.2	Sequential extraction procedures SEP 1 and SEP 2 used for selenium fractionation in this study.....	122
Figure 6.3	Depth profiles of redox potential and pH (mean \pm SE) of Red Beach sediment cores collected in April 2004 (Cores B1-6, top row) and July 2005 (Cores C1-4, bottom row).	124
Figure 6.4	Depth profiles of porewater sulfate (top row) and phosphate (bottom row) in four individual Red Beach cores: C1-C4.....	126
Figure 6.5	Porewater selenium concentrations (mean \pm SE) in Red Beach cores collected in April 2004 (Cores B1-6) and July 2005 (Cores C1-4), in comparison to the total solid-phase selenium in the corresponding cores...	128
Figure 6.6	Concentrations (% d.w.) of Total Carbon, Total Organic Carbon, Total Nitrogen, Total Sulfur, Acid Volatile Sulfides and Chromium Reducible Sulfur (pyrites) in Red Beach whole sediment: Cores C1-C4.....	130
Figure 6.7	Cluster relationships between sediment macrocomponents, porewater selenium, porewater sulfate and $< 63 \mu\text{m}$ fraction in Cores C1-C4.....	133
Figure 6.8	Macrocomponent ratios for Red Beach sediment cores (C1-C4, mean \pm SE). Top row: Ratios of TC to TOC, AVS, CrRS and TS. Bottom row: Ratios of TOC to TN, AVS, CrRS and TS.....	135
Figure 6.9	Selenium concentrations ($\mu\text{g/g}$ d.w.) in different sediment fractions of Cores B1-6.....	137
Figure 6.10	Selenium fractionation patterns (SEP 1) in Red Beach sediment cores (Cores B1-6), as percentages of the total selenium extracted from sediments.....	138
Figure 6.11	Selenium concentrations ($\mu\text{g/g}$) in different sequential extracts (SEP 2) of four Red Beach cores (whole sediments).....	141
Figure 6.12	Fractionation patterns (SEP 2) of selenium and co-extracted trace elements in Red Beach cores (mean of C1-C4).....	142
Figure 6.13	Comparison of selenium and sulfur Eh-pH diagrams. The stability region of water is between the two solid lines.....	148

Figure A.1	Dendrograms showing correlation patterns of selenium and common trace metals in whole (left) and > 250 μm (right) fractions of surface sediments from Port Kembla Harbour, excluding Site 20.....	VI
Figure A.2	Dendrograms (hierarchical clustering analysis) of selenium and common trace metals in 63-250 (left) and <63 μm (right) fractions of Port Kembla Harbour surface sediments.....	VII
Figure B.1	Grain size distribution in Cores B1-B6 collected in April 2005.....	XXVI
Figure B.2	Grain size distribution in Cores C1-C4, collected in July 2005.....	XXVII
Figure B.3	Porewater selenium and total selenium in individual Red Beach cores: B1-B6, collected in April 2004.....	XXVIII
Figure B.4	Porewater selenium and total selenium in individual Red Beach cores: C1-C4, collected in July 2005.....	XXIX
Figure B.5	Selenium concentrations ($\mu\text{g/g d.w.}$) in labile fractions of Cores B1-6....	XXX
Figure B.6	Selenium fractionation patterns (SEP 1) in individual Red Beach cores (B1-B6), Port Kembla Harbour.....	XXXI
Figure B.7	Selenium fractionation patterns (SEP 2) in individual Red Beach cores (C1-C4), Port Kembla Harbour.....	XXXII

List of Tables

Table 2.1	Some selenium compounds and their uses.....	9
Table 2.2	Common selenium minerals and their relative concentrations of selenium..	12
Table 2.3	Concentrations of selenium in Australian waters.....	14
Table 2.4	Concentrations of selenium in Australian sediments.....	15
Table 2.5	Concentrations of selenium in Australian marine organisms.....	18
Table 2.6	Biological effects of selenium in aquatic environments.....	24
Table 2.7	Common selenium species found in the environment.....	29
Table 3.1	Comparison of techniques for quantitative analysis of selenium in environmental samples.....	35
Table 3.2	HG-AAS operating conditions used in this study.....	42
Table 3.3	Acid extractable selenium from reference materials and test sediments using microwave digestion at 90 °C for 20 minutes.....	43
Table 3.4	Recoveries of acid extractable selenium from reference materials using two digestion procedures: USEPA Method 3051 and Zhou et al. (1997).....	44
Table 3.5	Efficiency of selenate reduction to selenite using HCl (microwave heating at 90 °C for 10 min, mean \pm SE, n=3).....	46
Table 3.6	Comparison of selenite recoveries (mean \pm SE) in aqua regia digestion with and without the selenate reduction step.....	47
Table 3.7	Recoveries of selenite spikes in nitrogen oxides-containing samples with urea addition.....	48
Table 3.8	Analytical performance for analysis of total selenium in sediment extracts by HG-AAS.....	49
Table 4.1	Selenium speciation in soil/sediments by HG-AAS traditional method and modern hyphenated techniques.....	53
Table 4.2	Selected hyphenated methods in recent literature for selenium speciation in water samples.....	55

Table 4.3	Major constituents and selenium concentrations in oxic and anoxic reference materials and test samples.....	58
Table 4.4	Extractant reagents tested and sediment phases extracted.....	60
Table 4.5	Optimized HPLC conditions.....	61
Table 4.6	Analytical performance for selenium speciation by HPLC and HG-AAS...	70
Table 5.1	Recoveries of aqua regia extractable metals from certified reference materials analysed by ICP-OES.....	81
Table 5.2	Correlations (r) between selenium and common trace metals in different grain size fractions of surface sediments from Port Kembla Harbour sampling sites, including Red Beach area.....	91
Table 5.3	Correlations (r) between selenium and other trace elements in Red Beach sediment (<63 µm) Cores A1-A3.....	103
Table 6.1	Common sequential extraction procedures employed in the literature to extract selenium from soils/sediments.....	109
Table 6.2	Summary of core samples collected for selenium fractionation studies.....	116
Table 6.3	Correlations (r) between total selenium concentrations and measured sediment parameters in Cores C1-C4.....	132
Table A.1	GPS, pH and grain size data for surface sediment samples collected on 7 April 2003.....	II
Table A.2	Trace element concentrations (µg/g) in different grain size fractions (µm) of surface sediment samples.....	III
Table A.3	Correlations (r) between selenium and common trace metals in different grain size fractions of surface sediments from Port Kembla Harbour sites, excluding Red Beach area (Sites 18, 19 and 20).....	V
Table B.1	Summary of all core samples.....	IX
Table B.2	pH values of core samples.....	X
Table B.3	Redox potentials (mV) of core samples.....	XI
Table B.4	Percentage grain size of <63 µm, 63-250 µm and >250 µm fractions in sediment A, B and C cores.....	XI

Table B.5	Porewater sulfate and phosphate concentrations (mg/L) in Cores C1-C4. Total porewater volume extracted (mL) vs the sample solid wt. before the porewater extraction (g) are included for information.....XII
Table B.6	Porewater selenium concentrations (µg/L) in Cores B1-B6 and C1-C4.....XII
Table B.7	Sediment macrocomponent concentrations (% dry wt, whole sediment) in Cores C1-C4.....XIII
Table B.8	Total selenium concentrations (µg/g, d.w.) in different grain sizes of the sediment A, B and C cores.....XIV
Table B.9	Concentrations of selenium (µg/g, d.w.) in sequential fractions (SEP 1) of Cores B1-B6 samples (< 63 µm sediment).....XV
Table B.10	Concentrations of selenium (µg/g, d.w.) in sequential fractions (SEP 2) of Cores C1-C4 samples (whole sediment).....XVI
Table B.11	Concentrations of chromium (µg/g, d.w.) co-extracted in the sequential extracts (SEP 2) of Cores C1-C4 samples.....XVII
Table B.12	Concentrations of copper (µg/g, d.w.) co-extracted in the sequential extracts (SEP 2) of Cores C1-C4 samples.....XVIII
Table B.13	Concentrations of iron (µg/g, d.w.) co-extracted in the sequential extracts (SEP 2) of Cores C1-C4 samples.....XIX
Table B.14	Concentrations of manganese (µg/g, d.w.) co-extracted in the sequential extracts (SEP 2) of Cores C1-C4 samples.....XX
Table B.15	Concentrations of nickel (µg/g, d.w.) co-extracted in the sequential extracts (SEP 2) of Cores C1-C4 samples.....XXI
Table B.16	Concentrations of lead (µg/g, d.w.) co-extracted in the sequential extracts (SEP 2) of Cores C1-C4 samples.....XXII
Table B.17	Concentrations of zinc (µg/g, d.w.) co-extracted in the sequential extracts (SEP 2) of Cores C1-C4 samples.....XXIII
Table B.18	Concentrations of total trace metals (µg/g, d.w.) in < 63 µm fractions of Cores A1-A3 samples.....XXIV
Table B.19	Concentrations of trace metals (µg/g, d.w.) co-extracted in the reactive iron fraction of Cores C1-C4 samples.....XXV
Table B.20	Sediment macrocomponent ratios (weight ratio, unless indicated) of Red Beach cores (C1-C4).....XXVI

Table B.21	Correlations (r) between sediment parameters and co-extracted elements in the soluble and adsorbed fraction of Cores C1-C4.	XXVIII
Table B.22	Correlations (r) between sediment parameters and co-extracted elements in the organically bound selenium fraction of Cores C1-C4.	XXIX
Table B.23	Correlations (r) between sediment parameters and co-extracted elements in the elemental selenium fraction of Cores C1-C4.	XXX
Table B.24	Correlations (r) between sediment parameters and co-extracted elements in the organic matter and sulfide fraction of Cores C1-C4.	XXXI
Table B.25	Correlations (r) between sediment parameters and co-extracted elements in the residual fraction of Cores C1-C4.	XXXII

Abbreviations

μg	Microgram
μL	Microlitre
ANSTO	Australian Nuclear Science and Technology Organization
AVS	Acid Volatile Sulfide
BCR	Community Bureau of Reference
BDL	Below Detection Limit
CrRS	Chromium Reducible Sulfide
dMedSe	Dimethyldiselenide
dMeSe	Dimethylselenide
Eh	Redox potential
GF-AAS	Graphite Furnace-Atomic Absorption Spectrometry
HG-AAS	Hydride Generation-Atomic Absorption Spectrometry
HPLC	High Performance Liquid Chromatography
hr	Hour
HS	Humic substance
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
KOAc	Potassium Acetate
kPa	Kilopascal
K_{sp}	Solubility product
LOD	Limit of Detection
MeOH	Methanol
mV	Millivolt
NA	Not analysed
NaOAc	Sodium Acetate
ND	Not Detected
NIST	National Institute of Standards and Technology
NRCC	National Research Council of Canada
NS	No sample
pK_{a}	Log acid dissociation constant

PKC	Port Kembla Copper Limited
PKPC	Port Kembla Port Corporation
PW	Porewater
PZC	Point of Zero Charge
RNAA	Radiochemical Neutron Activation Analysis
RPC	Reversed Phase Chromatography
RSD	Relative Standard Deviation
SAX	Strong Anion Exchange
SE	Standard Error
SeCys	Selenocysteine
SeCys ₂	Selenocystine
SeCyst	Selenocystamine
SeEt	Selenoethionine
Se ^{IV}	Selenite
SeMet	Selenomethionine
SEP	Sequential Extraction Procedure
SeU	Selenourea
Se ^{VI}	Selenate
TC	Total Carbon
TFE	Tetrafluoroethylene
TMAH	Tetramethylammonium hydroxide
TMeSe	Trimethylselenonium
TN	Total Nitrogen
TOC	Total Organic Carbon
TS	Total Sulfur
UC	University of Canberra
XAS	X-Ray Absorption Spectrometry
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence Spectrometry